DIFLUORAMINE : AN INFRARED STUDY OF THE COMPLEXES

BETWEEN DIFLUORAMINE AND THE ALKALI METAL FLUORIDES

By H. E. Dubb, R. C. Greenough, and E. C. Curtis

(ABSTRACT)

Difluoramine, HNF_2, was condensed on alkali metal fluoride optical crystals and the infrared spectra of the resulting compounds were measured. Complex formation was observed with KF, RbF, and CsF. An analysis of the infrared spectra indicates that two compounds may be formed, one a simple hydrogen bonded complex, and the other a new species $MNF_2 \cdot HF$.

INTRODUCTION

Potassium, rubidium, and cesium fluorides form complexes with difluoramine (that dissociate reversibly) when the latter is condensed onto these materials. When the potassium and rubidium complexes are allowed to warm to room temperature they react further to form the cis and trans difluorodiazine isomers and the alkali metal bifluorides. The cesium complex explodes before reaching room temperature.[1]

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1. Lawton, E. A., D. Pilipovich, and R. D. Wilson, U. S. Patent 3,109,711 (Nov. 5, 1963).

It has been postulated that the explosive nature of the cesium complex as contrasted with the nonexplosive nature of the potassium and rubidium

complexes might be due to the formation of a highly unstable difluoramide ion, NF_2^-. The present infrared study of the structures of these complexes was undertaken with the purpose of determining whether such an ion does exist.

Infrared spectra of the complexes were obtained by condensing difluor-amine onto optical blanks of the alkali metal fluorides at -95 C and scanning through the rock salt region with a Beckman IR-7 spectrometer. Examination of the spectra indicates that potassium and rubidium fluorides primarily form hydrogen bonded complexes of the structure $M^+F^-\cdot HNF_2$ with possibly small amounts of a difluoramide complex, $M^+\cdot FH\cdot NF_2^-$, also present. Cesium fluoride seems at first to form a complex with two (or more) moles of difluoramine. On pumping this is converted to a mixture of $Cs^+F^-\cdot HNF_2$ and $Cs^+\cdot FH\cdot NF_2^-$. The evidence for the existence of a difluoramide ion is strongest in the case of cesium.

EXPERIMENTAL

The difluoramine was prepared by the action of concentrated sulphuric acid on fluorinated urea. It was then purified by distillation under a vacuum at reduced temperatures.[2] The potassium and cesium fluoride crystals

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2. Lawton, E. A., and J. Q. Weber, J. Am. Chem. Soc. 81, 4755 (1959), E. A. Lawton and D. F. Sheehan unpublished work.

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were obtained from the Harshaw Chemical Co. and the rubidium fluoride from Semi-Elements, Inc.

The alkali fluoride single crystal was mounted on a copper block inside an infrared cell fitted with rock salt windows. Gaseous difluoramine was condensed onto a 1" x 1" optical blank of the appropriate alkali metal fluoride maintained at about -95 C by a slush bath of methylcyclohexane. The copper block was in contact with the slush coolant so that the alkali fluoride plates could be kept at the proper temperature, which was measured with a copper-constantan thermocouple. The apparatus will be described in detail elsewhere.[3]

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3. Bell, R. E., R. C. Greenough, G. Brull, Jr., and H. E. Dubb, to be published.

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There was considerable difficulty in handling the crystals since they are very hygroscopic. The crystals were polished on a felt cloth wet with a butanol solution saturated with the appropriate salt, and then were mounted on the copper block and sealed into the infrared cell. All these manipulations were done inside a very carefully constructed dry box with a 97% Ar - 3% H_2 atmosphere maintained at a positive pressure so that the alkali fluoride plate was not exposed to air at any time.

The difluoramine was admitted through a nozzle directly onto the plate. Actually, the vapor pressure of difluoramine is high enough so that a portion of the gas condensed on the copper block; however, most of it did condense on the window. The spectra of the resulting complexes were then scanned with a Beckman IR-7 spectrometer set at low resolution and high speed. The machine was not especially calibrated for this experiment, but it is felt that frequencies reported are good to ± 2 cm^{-1} at 1000 cm^{-1} and ± 20 cm^{-1} at 3000 cm^{-1}.

At the end of the experiment the potassium and rubidium fluoride plates were allowed to warm and the spectrum of the bifluoride salt was detected on the plates by comparison with the known KHF_2 spectrum[4]. The cesium fluoride blank was destroyed at the end of the experiment by condensing

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4. J. A. A. Ketelaar and W. Vedder, J. Chem. Phys. 19, 654 (1951).

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methanol onto the plate to avoid an explosion and subsequent harm to the apparatus when it was warmed to room temperature.

There was some difficulty with leaks with this apparatus; even a very small amount of water on the alkali fluoride plates gives a very intense band at 3200 cm^{-1}.

<center>RESULTS</center>

The spectra of HNF_2 on KF and HNF_2 on CsF are shown in Figure 1. The spectrum of HNF_2 on RbF was very similar to that on KF. An assignment of all spectra measures is given in Table I. A spectrum of liquid HNF_2 on NaCl was also measured. Bands appeared at approximately the same frequencies as the gas phase bands.

There was some air leakage into the cell during the KF and CsF experiments, raising some doubt about the HF frequency. It is felt that absorption around 3500 cm^{-1} was not due to water but was caused by a HF stretching mode. This assignment was more certain in the case of the CsF complex.

KF and RbF seem to form similar complexes. The N-H stretching frequency at 2600 cm^{-1} is shifted down 600 cm^{-1} from the gas phase frequency. The N-H stretching band in the complex is considerably more intense than the same band in the gas phase.[5] The other vibrational modes are at

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5. J. J. Comeford, D. E. Mann, L. J. Schoen, and D. R. Lide, J. Chem. Phys. 38, 461 (1963).

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about the same frequencies as in the gas phase spectrum. The probable structure of this complex is shown in Figure 2 as Form A, and seems to be that of a strongly hydrogen-bonded complex. It is possible that some $M^+ \cdot FH \cdot NF_2^-$ complex exists also but if this is so, its concentration is smaller than in the CsF case.

The spectrum of the CsF complex is somewhat more complicated in agreement with the fact that evidence for two complexes has been reported.[6]

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6. E. A. Lawton, D. Pilipovich, and R. D. Wilson ~~to be published~~. in press, J. Inorg. Chem.

The bands in the early spectrum (labeled complex plus gas) are shifted even further from the gas phase frequencies than in the KF and RbF cases. The increased complexity of the NH stretching frequencies supports the existence of at least two types of complexes, but hardly permits speculation on their exact structure. On pumping off the excess gaseous HNF_2 the spectrum is simplified and all bands shift to the blue indicating that the complex is now of a single type very probably one mole of CsF to one mole of HNF_2. A new band appears at 720 cm^{-1} and one at 3500 cm^{-1}.

These bands can be accounted for by an NF_2^- ion and HF. It would appear that here also two types of complexes are present, one a hydrogen bonded complex similar to the $KF \cdot HNF_2$ and the second complex containing the difluoramide ion, $Cs^+ FH \cdot NF_2^-$ (Fig. 2, Form B).

An attempt was also made to find the bending mode of the NF_2^- ion which should be shifted well to the blue from the 500 cm^{-1} frequency in HNF_2. This would have proved the existence of an NF_2^- ion, but unfortunately the CsF plate was opaque in this region and an attempt to deposit CsF powder on a AgCl window was unsuccessful as there was too much light scattering from the powder.

Discussion

This data provides possibly the best indication to date that a NF_2^- ion exists. The evidence for the existence of the NF_2^- ion is more conclusive for $Cs^+ \cdot FH \cdot NF_2^-$ than for $K^+ \cdot FH \cdot NF_2^-$ or $Rb^+ \cdot FH \cdot NF_2^-$. The CsF 1:1 complex can be pictured as a mixture of two tautomeric forms where the hydrogen resides in one of two potential energy minima, one corresponding to $Cs^+ F^- \cdot HNF_2$ and the other to $Cs^+ \cdot FH \cdot NF_2^-$ (Figure 3a). The KF and RbF complexes are of the same type as the CsF complex but with less favorable potential energy minima for their NF_2^- ion forms. In fact, it is not certain that they contain such minima (Figure 3b). The evidence seems only slightly to favor their existence. Since both forms of the CsF complex were observed in the spectrum, they must have an interconversion rate which is slow compared to the measuring infrared frequencies of about 10^{14} cps.

When there was excess gaseous HNF_2 in contact with CsF additional absorptions were observed in the N-H stretch region. This indicated that more then one HNF_2 may be complexed with each CsF entity. When the higher complex was present, no evidence of NF_2^- ion was found in the spectrum. Thus the NF_2^- ion may not exist except under exceptionally favorable conditions.

Even though the existence of NF_2^- ion is indicated by this work, this should in no way encourage a belief that it might be found in other systems; both the driving force of forming an HF bond and the positioning of the HNF_2 in the $M^+F^- \cdot HNF_2$ complex would seem to provide the best possible conditions for forming and stabilizing NF_2^- ion.

ACKNOWLEDGEMENTS
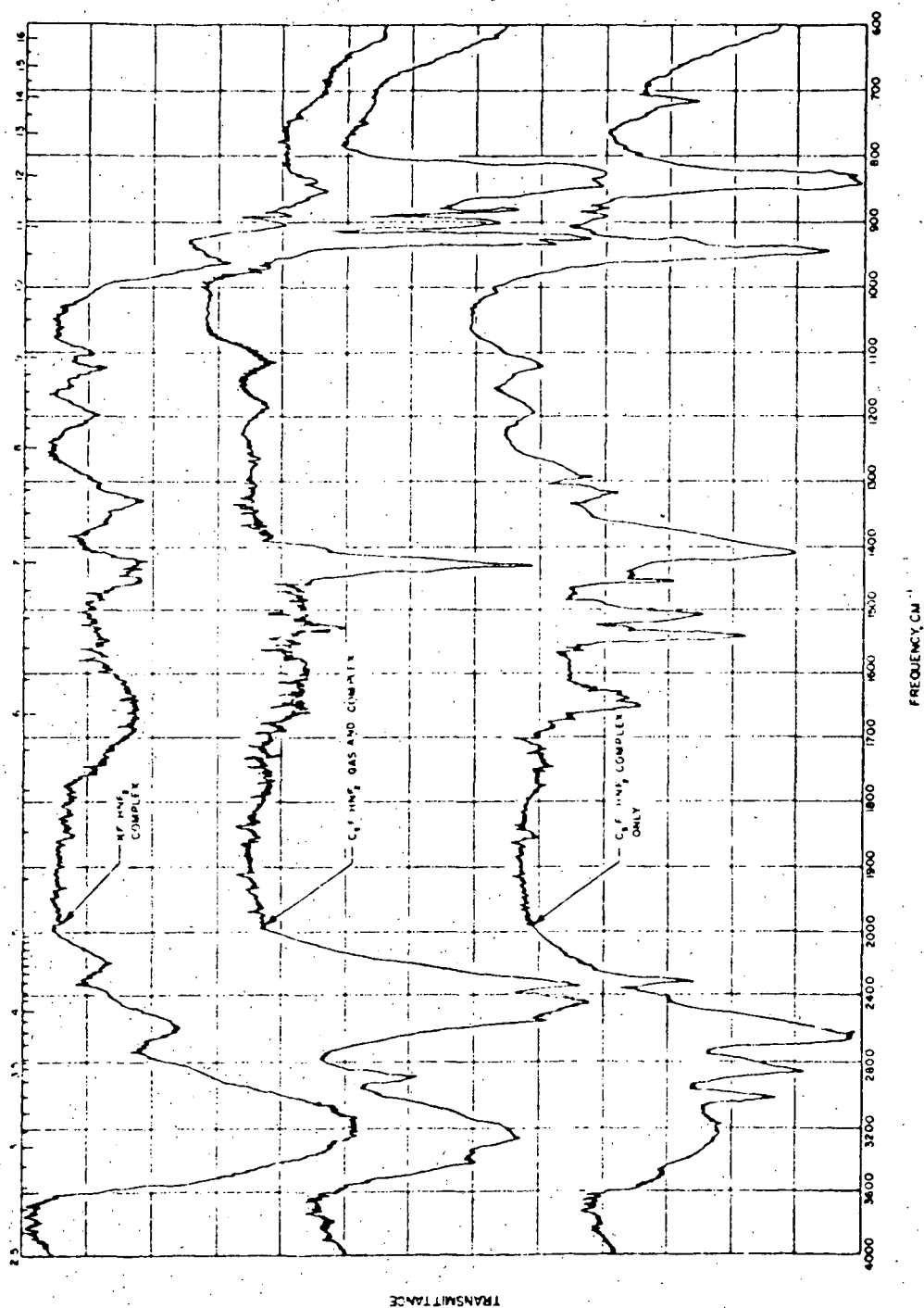
Fig. 1.–INFRARED SPECTRA OF THE DIFLUORAMINE/ALKALI-METAL FLUORIDE COMPLEXES

Table 1.-ASSIGNMENTS OF INFRARED SPECTRA

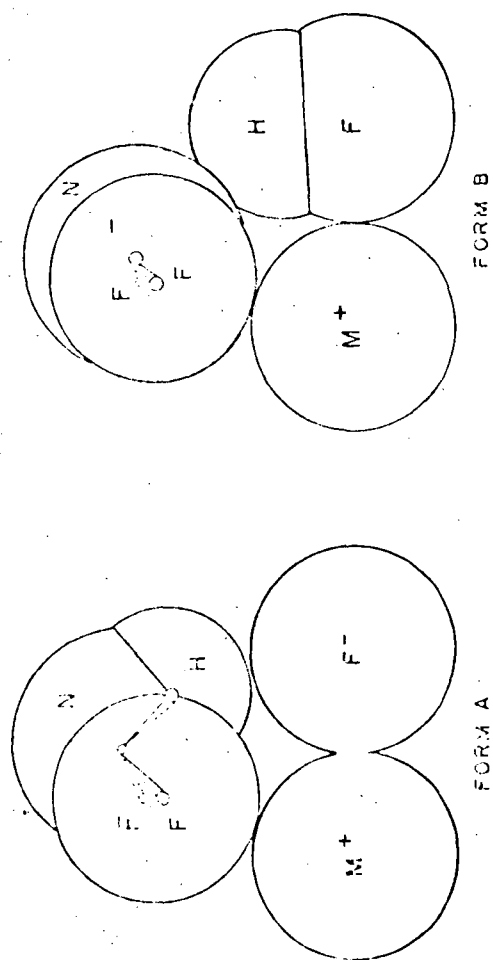| Assignment	INF$_2$ Gas and HF Cold Film	KF + INF$_2$	RbF + INF$_2$	CsF + INF$_2$ Complex + Gas	CsF + INF$_2$ Pumped On Complex
			Frequency, cm^{-1}		
HF Stretch	3400 3100		3300b?		3500? 3200?
NH Stretch	3195w	2900? 2850? 2600	2850? 2600 2450?	2850 2650 2500?	2900 2450 2550
NH Bend (asymmetric)	1424s	1410	1440	1510	1545
NH Bend (symmetric)	1307s	1520		1410	1460 1432
NF Stretch (symmetric)	972s	965	960	942	942 930
NF Stretch (asymmetric)	888vs	850 830	850	850	840 825
Liquid and Ionic	800	800	800		
NF Stretch	700	700	700	720	720

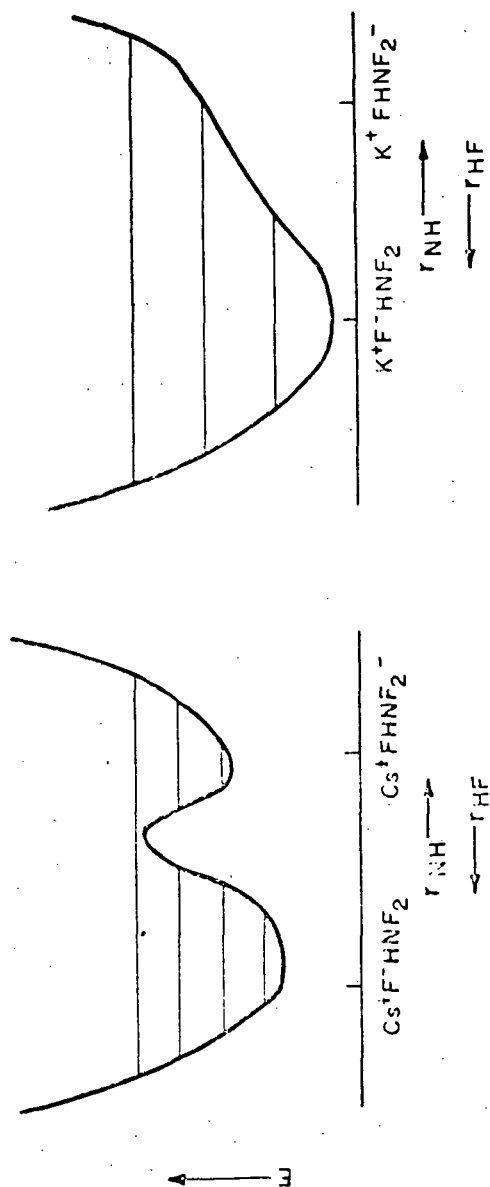Fig. 2.--APPROXIMATE SCALE DRAWING OF THE HNF$_2$ COMPLEXES

Fig. 3.–POTENTIAL ENERGY OF THE COMPLEX AS A FUNCTION
OF THE POSITION OF THE HYDROGEN ATOM